

PATENT SPECIFICATION

NO DRAWINGS

967,879

967,879



Date of Application and filing Complete Specification July 5, 1962.

No. 25825/62.

Application made in United States of America (No. 122080) on July 6, 1961.

Complete Specification Published Feb. 19, 1964.

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Index at acceptance: —C5 E(12C, B1A, B1N)

International Classification: —C 07 c

COMPLETE SPECIFICATION

Improvements in or relating to the Hydrogenation of Olefins in the Presence of Aromatic Hydrocarbons

We, ENGELHARD INDUSTRIES, INC., a corporation organized under the laws of the State of Delaware, United States of America, of 113 Astor Street, Newark, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the hydrogenation of olefins in the presence of aromatic hydrocarbons, and is concerned, more particularly but not exclusively, with a method whereby diolefin hydrocarbons can be substantially

15 hydrogenated when admixed with monoolefin hydrocarbons and aromatic hydrocarbons, without substantial hydrogenation of the aromatic hydrocarbons. In a more limited aspect, the invention is concerned with a method

20 whereby both diolefin hydrocarbons and monoolefin hydrocarbons can be substantially hydrogenated when admixed with aromatic hydrocarbons without substantial hydrogenation of the aromatic hydrocarbons.

25 Normally liquid hydrocarbon mixtures which contain diolefins, monoolefins and aromatics can be produced by a variety of processes which are known in the art. Such processes can involve the pyrolysis or cracking of crude petroleum or fractions derived therefrom containing at least two carbon atoms on the average, for example ethane, propane, propylene, butane, natural gasoline, light

30 straight run gasoline (for example, one having a boiling range of from 90 to 215° F.), straight run naphtha (for example, one having a boiling range of from 215 to 430° F.), kerosene, naphthenic catalytic light cycle stock produced in the cracking of gas oil by the fluid process to produce gasoline and straight

40 run gas oil. The aforementioned pyrolysis operations can be carried out with or without the aid of a catalyst and in the presence or

absence of steam. Generally, they are carried out at temperatures within the range of 1350° F. to 1550° F., although somewhat lower and somewhat higher temperatures can also be used, and at pressures within the range of from zero psig to fifty psig although in some instances considerably higher pressures can be used. The pyrolysis operations are generally carried out primarily for the production of ethylene, the normally liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics being obtained as a by-product. The normally liquid hydrocarbon mixtures which are hydrogenated in accordance with the method of the invention will have a boiling point at atmospheric pressure in the range of from 100° F. to 400° F.

Materials which can be subjected to the hydrogenation operations of the present invention include dripolene or fractions thereof. Dripolene is a normally liquid mixture of hydrocarbons obtained as a by-product in the high temperature pyrolysis of normally gaseous hydrocarbons to produce ethylene. In the production of dripolene, a gaseous hydrocarbon such as ethane, propane, propylene or a mixture thereof (for example, by-product refinery gas) is pre-heated and passed through an alloy tube at a high space velocity and at a pyrolysis temperature between 1200° F. and 1800° F., preferably between 1350° F. and 1550° F. Low pressures up to 85 psig are ordinarily employed in this operation, a pressure below 20 psig being satisfactory. The time of exposure to the high temperature is usually 0.05 to 5 seconds, contact times of 0.1 to 1 second being preferred.

The pyrolysis produces normally gaseous products containing unsaturated hydrocarbon such as ethylene, normally liquid hydrocarbons rich in unsaturated hydrocarbons including olefins and diolefins of vary boiling points and structural configuration, and various aromatic

[Price 4s. 6d.]

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hydrocarbons, as well as tar. The unsaturated hydrocarbons such as ethylene which are contained in the normally gaseous product are usually the desired product of the pyrolysis process. The normally liquid hydrocarbons and tar which are obtained are considered to be by-products of the pyrolysis operation. High temperature pyrolysis products are rapidly cooled, usually by quenching with water to a temperature of about 400° F. A viscous tarry material condenses out of the gas during the quenching. The gases from the quenching operation are compressed and cooled and a liquid material which boils at a temperature in the range 100° to 400° F. condenses out of the gases during the compressing-cooling step. This liquid is dripolene. The amount of tar and dripolene produced is dependent upon the feed, temperature, contact time and pressure. The quantity of liquid hydrocarbons produced in this way is ordinarily about 3 per cent by weight of the total quantity of gas charged to the pyrolysis reactor. As a charge stock to the hydrogenation method of this invention, it is desirable to use an overhead cut or fraction taken in a distillation of the total dripolene, such cut or fraction being generally free of those high boiling fractions of the dripolene which have heretofore been used in the manufacture of resins by thermal or catalytic polymerization. The dripolene overhead cut will generally have a boiling point at atmospheric pressure not exceeding 375° F. and will generally amount to not more than 90 per cent by volume of the dripolene from which it has been obtained by distillation. Potential resin-forming ingredients present in the dripolene can also be removed from the dripolene by passing it through a bed of activated alumina at room temperature.

As has been stated, the normally liquid hydrocarbon mixtures which are hydrogenated in accordance with the invention contain two types of hydrocarbons which are desirable motor fuel ingredients, namely, monoolefins and aromatics, and one type which are not, namely diolefins. Diolefins are undesirable motor fuel ingredients because they are unstable and lead to gum formation. In its broadest aspect, the present invention provides a method whereby the diolefins can be hydrogenated, so that the hydrogenated product contains monoolefins and a large proportion of the aromatics originally present in the hydrocarbon mixture subjected to hydrogenation. When this is done, the hydrogenated normally liquid hydrocarbon mixture is upgraded in its utility as a motor fuel ingredient.

The normally liquid hydrocarbon mixtures which are employed as a starting material are a valuable source of aromatics. Aromatics are conventionally recovered from mixtures containing them by the use of solvent extraction procedures. For such procedures to be used

most advantageously, the mixtures subjected to extraction should be essentially free from both diolefins and monoolefins, since the presence of such olefins interferes with the solvent extraction. In a more limited aspect, the present invention provides a method for the substantially complete hydrogenation of both diolefins and monoolefins.

It has heretofore been proposed (see also U.S. Patent No. 2,953,612, U.S. Patent No. 2,799,627) to hydrogenate aromatic-containing hydrocarbon fractions to remove diolefins and monoolefins therefrom using a platinum-alumina or palladium-alumina catalyst. In accordance with the method of the present invention, there is employed a palladium-alumina catalyst, the use of this type of catalyst making for selectivity. In other words, by using a palladium-alumina catalyst there is obtained less hydrogenation of aromatics, in comparison with the amount of aromatics hydrogenation which takes place when a platinum-alumina catalyst is used. Moreover, in order to minimize the hydrogenation of aromatics and also to provide for long catalyst life, the hydrogenation is conducted at a temperature not exceeding 210° F. Furthermore, in the method of the present invention using the palladium-alumina catalyst, the hydrogenation is carried out with the dripolene or other hydrocarbon mixture being hydrogenated at least 90 per cent by weight in the liquid phase while the hydrocarbon mixture undergoing hydrogenation is contacted with the catalyst. In the process described in U.S. Patent No. 2,953,612, although when the dripolene first contacts the catalyst it is almost entirely in the liquid phase, the dripolene vaporizes during operation as a result of the heat generated by the hydrogenation, so that in its later stages the operation is a vapor phase hydrogenation. In the operation described in U.S. Patent No. 2,799,627, the hydrogenation is a vapor phase one.

The catalyst which is used in practicing the method of the invention is one which consists essentially of palladium supported on an activated or gamma-alumina base, preferably a base which is essentially free of components which react with alumina to form an acid catalyst such as chlorine, fluorine, silica and boria. The catalyst will generally contain from 0.05 to 10.0 per cent by weight of palladium, preferably from 0.1 to 1.0 per cent by weight and preferably deposited on the superficial surface of the alumina. Preferably, the base will be of relatively high surface area, for example, from 25 to 500 square meters per gram or higher as measured by the BET method. Catalysts which can be utilized in the present method are well-known in the art. For example, suitable catalysts can be prepared by impregnating commercially available activated alumina pellets with an aqueous solution of a suitable palladium salt, for example, palla-

dium chloride admixed with hydrochloric acid, followed by precipitation of the palladium in situ by the use of aqueous hydrogen sulfide solution or gaseous hydrogen sulfide. After this has been done, the pellets can be dried and calcined in air. Catalysts suitable for use in the method can also be prepared by the general procedure described in Specification No. 624353.

The hydrocarbon mixture hydrogenated will generally have a bromine number (ASTM-D-1158-55T) of at least 10, and generally in the range of from 30 to 100. In the aspect of the invention wherein the diolefins are hydrogenated to provide a reaction product containing monoolefins and aromatics, the hydrogenation can be carried out under a wide variety of operating conditions, depending upon the particular stock being treated, the intended use of the product and the activity of the catalyst used. In general, however, the hydrogenation will be conducted at a pressure in the range of from zero psig to 2000 psig (preferably 100 psig to 700 psig) and at a liquid hourly space velocity (LHSV, meaning volume of hydrocarbon mixture being hydrogenated per volume of catalyst per hour) in the range of from 0.1 to 10. The amount of hydrogen introduced into the reaction zone will generally be from 2 to 20 times that required to saturate completely the olefins (monoolefins plus diolefins) present in the feed being hydrogenated.

As has been stated above, the hydrogenation with the palladium-alumina catalyst is carried out at a temperature not exceeding 210° F., and generally at a temperature in the range of from 100° F. to 200° F. Under adiabatic conditions, the temperature of the reaction mixture rises as the hydrogenation proceeds. In order to prevent undue temperature increase of the mixture undergoing hydrogenation, various means can be resorted to. For example, the hydrocarbon undergoing hydrogenation can be admixed with an extraneous inert material, for example the hexane used in the examples below, or with recycled hydrogenated product. On the other hand, the reaction zone can be supplied with cooling means, for example a cooling jacket or coils, or the catalyst can be disposed in two or more beds with cooling means being provided between the beds.

As has been stated, one aspect of the invention involves the production of a hydrogenated product which is essentially free from both diolefins and monoolefins, that is, has a bromine number not exceeding one. This can be accomplished, in accordance with the invention, by subjecting the product resulting from the hydrogenation step involving the use of palladium-alumina catalyst to vapor phase hydrogenation using a catalyst which consists essentially of cobalt molybdate supported on alumina. When the hydrogenation step with

cobalt molybdate is carried out, the hydrogenated product produced in the preceding step is preferably treated in order to remove polymers. This can be accomplished in a variety of ways, for example by distilling and discharging the bottom. On the other hand, the hydrogenated product from the first step can be passed through a bed of activated alumina at room temperature.

Various methods for manufacturing cobalt molybdate supported on alumina catalysts are known in the art. Note, for example, U.S. Patent No. 2,325,033 and U.S. Patent No. 2,898,308. Such catalysts generally consist essentially of from 2 to 5 per cent by weight of cobalt oxide and from 5 to 15 per cent by weight of molybdic oxide, the balance being alumina. In using the cobalt molybdate-alumina catalyst, temperatures in the range of from 550 to 950° F., pressures in the range of from 200 to 1000 psig, and weight hourly space velocities (WHSV, meaning weight units of hydrocarbon feed to be hydrogenated per weight unit of catalyst per hour) in the range of from 0.1 to 10 can suitably be used. Hydrogen to hydrocarbon ratios in the range of from 1 to 10 can be employed, these ratios being on a molar basis and on the basis of hydrocarbons introduced into the reaction zone. Tungsten-nickel sulfide, nickel-alumina, platinum-alumina and palladium-alumina can be used in place of the cobalt molybdate-alumina catalyst.

The following Example illustrates the invention.

EXAMPLE

A quantity of commercially activated alumina was first obtained. This sample was of 8-14 mesh size (U.S. Standard Sieve), had a surface area of about 250 square meters per gram (BET method), and had the following analysis by weight; alumina 92 per cent; Na₂O, 0.80 per cent; Fe₂O₃, 0.12 per cent; SiO₂, 0.09 per cent and TiO₂, 0.01 per cent, the remaining being volatile matter.

This commercially activated alumina was employed in the manufacture of a catalyst containing 0.3 per cent by weight of palladium by making the catalyst in the manner described in Specification No. 624353.

A 0.500 inch outside diameter reactor tube with a 0.0049 inch wall was charged with 5 ml. or 4.1 grams of the palladium-alumina catalyst which was mixed with 19 ml. of corundum pellets of a size similar to that of the palladium-alumina catalyst. The reactor tube was surrounded with a liquified paraffin bath maintained at 158° F., and nitrogen gas was bubbled through the bath to equalize its temperature.

In this example a fraction obtained by fractionating a quantity of dripolene was hydrogenated. This fraction had a boiling range at atmospheric pressure of from 93° F. to 295° F., had a specific gravity (measured at

20° C. and referred to water at 4° C.) of 0.865, and had a bromine number of 50. The fraction contained 0.0045 per cent by weight of sulfur and analyzed as follows by volume:

5 isoprene, 0.5 per cent; cyclopentadiene, 9.2 per cent; cyclohexadiene, 1.3 per cent; benzene, 71.1 per cent; toluene, 17.0 per cent; xylene 0.6 per cent; and styrene 0.3 per cent.

10 As the dripolene fraction had been standing a considerable period of time before being used in this example, it was passed through a bed containing 65 ml. of the same kind of activated alumina as was used in preparing the

15 palladium-alumina catalyst. Prior to passage through the bed, the dripolene fraction was diluted with an equal volume of normal hexane.

In carrying out the hydrogenation, the dripolene fraction which was diluted with an equal volume of normal hexane and which had been passed through the bed of activated alumina was delivered as feed upward through the catalyst reactor bed at the rate of 10.0 ml. per hour (liquid volume hourly space velocity of one, based upon the dripolene fraction). Hydrogen was introduced cocurrently with the dripolene fraction at a rate of 2.40 liters per hour, measured at 25° C. and one atmosphere. A hydrogen rate of 0.32 liters per hour was necessary to hydrogenate all of the olefins present in the dripolene fraction. The reactor pressure was maintained at 400 psig with the hydrogen being delivered from a pressurized tank and with the dripolene fraction being

35 supplied by means of a pump. The bromine number of the hydrogenated product dropped to a low level during the first few hours of operation and then levelled off at 4—5 (8—10 on the basis of the dripolene fraction hydrogenated). This life study was continued for more than 2500 hours, indicating a favorable life for the palladium catalyst in selectively removing diolefins from the dripolene fraction.

45 A sample of the dripolene fraction-n-hexane mixture hydrogenated with the palladium-alumina catalyst was distilled to yield a fraction containing 46 per cent by volume of aromatics and 52 parts per million of sulfur. This distilled fraction had a bromine number of 4.3 and had the following ASTM distillation: initial boiling point, 148° F.; 10 per cent, 156° F.; 50 per cent, 163° F.; 90 per cent, 184° F.; and end point, 247° F.

55 The distillate fraction described in the preceding paragraph was hydrogenated over a cobalt molybdate-alumina catalyst at 5 WHSV and 500 psig. In carrying out this operation, the catalyst used was in the form of 1/16-inch pellets and analyzed approximately 3 per cent by weight of cobalt oxide and approximately 10 per cent by weight of molybdenic oxide, the remainder being alumina. Hydrogen

65 gas was introduced into the reaction zone at

the rate of five moles per mole of total hydrocarbon feed, including the n-hexane present therein. When the reaction temperature was 600° F., the hydrogenated product had a bromine number of 0.2. A reaction temperature of 700° F. was also found to be suitable for use in the hydrogenation step with the cobalt molybdate-alumina catalyst, inasmuch as essentially no hydrocracking or loss of aromatics occurred when the hydrogenation was conducted at this temperature.

WHAT WE CLAIM IS:—

1. A method for the hydrogenation of diolefins present in a normally liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics and boiling, at atmospheric pressure, in the range of from 100° F. to 400° F., which comprises contacting the hydrocarbon mixture and hydrogen with a palladium-alumina catalyst under hydrogenation conditions of pressure and space velocity and at a temperature not exceeding 210° F. whereby the diolefins present in the hydrocarbon mixture are hydrogenated, the hydrocarbon mixture being hydrogenated being at least 90 per cent by weight in the liquid phase at all times while it is in contact with the catalyst.

2. A method according to Claim 1, wherein the normally liquid hydrocarbon mixture is dripolene.

3. A method according to Claim 1 or 2, wherein the palladium-alumina catalyst consists essentially of activated alumina having supported thereon from 0.05 to 10 per cent by weight of palladium.

4. A method according to Claim 1, 2 or 3, wherein the pressure is in the range of from zero psig to 2000 psig and wherein the liquid hourly space velocity is in the range of from 0.1 to 10.

5. A method according to any one of Claims 1 to 4, wherein the hydrocarbon mixture containing hydrogenated diolefins is contacted in the vapor phase together with hydrogen with a cobalt molybdate-alumina catalyst under hydrogenation conditions of temperature, pressure and space velocity, whereby the monoolefins are hydrogenated without substantial hydrogenation of aromatics present in the hydrocarbon mixture.

6. A method according to Claim 5, wherein, in the first hydrogenation step, the pressure is within the range from zero psig to 2000 psig and the liquid hourly space velocity is within the range from 0.1 to 10 and wherein, in the second hydrogenation step, the temperature is within the range from 550 to 950° F., the pressure is within the range from 200 to 1000 psig and the weight hourly space velocity is within the range from 0.1 to 10.

7. A method according to any one of Claims 1 to 4, wherein the hydrocarbon mix-

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- ture containing hydrogenated diolefins is contacted in the vapor phase together with hydrogen with a tungsten-nickel sulfide catalyst, a nickel-alumina catalyst, a platinum-alumina catalyst or a palladium-alumina catalyst under hydrogenation conditions of temperature, pressure and space velocity, whereby the monoolefins are hydrogenated without substantial hydrogenation of aromatics present in the hydrocarbon mixture.
- 5 8. A method for the hydrogenation of diolefins and monoolefins present in a normally liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics and boiling, at atmospheric pressure, at a temperature in the range of from 100° F. to 400° F., substantially as described in the foregoing Example.
- 10 9. The product of the method claimed in any one of the preceding claims.

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PATENT SPECIFICATION

NO DRAWINGS

62879



967,81

Date of Application and filing Complete Specification July 5, 1962.

No. 25825/62.

Application made in United States of America (No. 177080) on July 6, 1962.

PATENTS ACT, 1949

SPECIFICATION NO. 967,879

In accordance with the Decision of the Superintending Examiner acting for the Comptroller-General, dated the 25th day of January, 1966, this Specification has been amended under Section 14 in the following manner:-

Page 2, line 92, page 4, line 87, *delete* "not exceeding" *insert* "in the range of from 100°F to".

Page 2, line 98, page 4, line 90, *for* "being" *read* "to be".

Page 2, lines 98 and 99, page 4, line 90, *after* "hydrogenated" *insert* "being passed concurrently with the hydrogen upwardly through the catalyst and being".

Page 2, lines 98 and 99, *delete* "while the hydrocarbon mixture undergoing hydrogenation is contacted" *insert* "whilst in contact".

Page 2, line 100, *after* "catalyst" *insert* "thereby flooding the catalyst".

Page 2, line 121, *for* "Preferably, the base" *read* "The base".

Page 2, line 122, *delete* "for example" *insert* "i.e.".

Page 2, lines 123 and 124, *delete* "or higher".

Page 3, lines 36 and 37, *delete* "not exceeding 210°F., and generally at a temperature".

Page 3, line 38, *for* "200°F." *read* "210°F."

Page 4, line 24, *after* "bed" *insert* "to flood the catalyst bed".

Page 4, line 85, *after* "catalyst" *insert* ", the alumina having a surface area in the range of from 25 to 500m²/g when measured by the BET method,".

Page 4, line 87, *for* "210°F." *read* "210°F.,".

Page 4, lines 88 and 89, *delete* whereby the diolefins are hydrogenated,".

Page 4, line 93, *after* "catalyst" *insert* "thereby flooding the catalyst, whereby the diolefins present in the hydrocarbon mixture are hydrogenated.".

THE PATENT OFFICE,
27th April, 1966.

D 69516/3

ERRATUM

SPECIFICATION NO. 967,879

AMENDMENT NO. 1

Page 4, line 87, *for* "temperautre" *read* "temperature".

THE PATENT OFFICE